Resonant Soft X-ray Emission Spectroscopy of Ni Complexes

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Transition metals, especially *3d* transition metals, are important active elements inside various biological molecules, performing different roles, such as catalysis, regulatory and electron transfer. Some important examples of biological nickel sites include the ones inside Ni-Fe hydrogenase, CO dehydrogenase and Acetyl Co-A synthetase. These enzymatic nickels are usually take different electronic structures in different enzymatic states and/or different chemical environments. In turn, electronic structure determines the properties and biological activities for these molecules. For example, accurate assignment for the NiFe hydrogenases' Ni oxidation and spin states in the active catalytic reaction circle will lead to a full understand of its biological mechanism.[1] So far the element-specific electronic structure in biological metals has been little investigated with soft X-rays, except for some studies using absorption spectroscopy (XAS).[2,3]

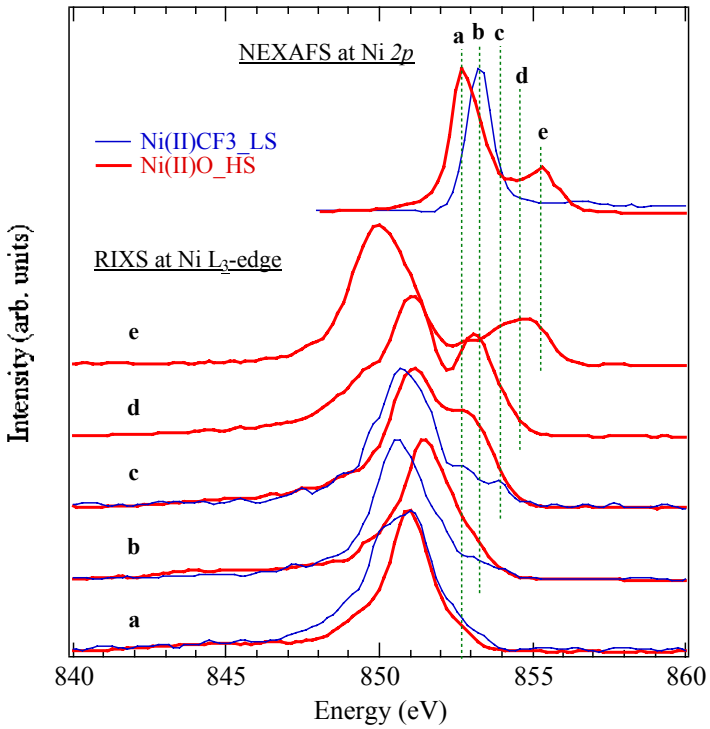
Ni complexes with different oxidation and spin states are investigated for long time due to different interest. The complexes of Ni(II) versus Ni(III) and low spin versus high spin Ni(II) are particularly interested due to their resemblance to some biological nickel states. For example, the as-isolated NiFe hydrogenase (Ni-A) has a Ni(III) site while the reduced active state (Ni-R) has a Ni(II) site. Whether the Ni-R has a low spin or high spin Ni-R is still in debate. SXES study of a series of Ni complexes with these oxidation states will pave the way to SXES study of real biological metals in the future. This is also true for other experimental methods developed in the past, including soft X-ray absorption spectroscopy, for studying biological metals.

Soft-x-ray transition originates from an electron transition between a localized core state and a valence state and the method is element specific. The strong interaction in between the core and the valence electron and the higher energy resolution makes it chemically sensitive and informative. However, Limitation exists for the soft absorption spectroscopy (XAS) when biology-related systems are studied. Usually these molecules have complicated and mixed oxidation states and spectral feature overlap is unavoidable, which makes XAS less accurate. On the other hand, the identification of each component is critical in understanding the electronic structure(s). The most striking features of using high-resolution soft-x-ray emission spectroscopy (SXES) is the selectivity in different absorption band. With SXES, interested site(s) in a mixed species (*e.g.* Ni(III) vs. Ni(II) or high spin-Ni(II) vs. low spin-Ni(II) peaks) can be individually, or at least preferentially excited and studies. Each component can then be identified when compared with theoretical calculation.

Due to the relative low fluorescence yield for the soft X-ray excited transitions and the lower efficiency of old spectrometer, the application of SXES is limited with old instruments. SXES has been subjected to a revived interest due to the new possibilities offered by the much higher brightness of the new generation of synchrotron radiation sources, the corresponding high performance beamline and instruments[4] and newer generation of high through-put and high

resolution spectrometer. Resonant SXES has been successfully applied to the studies of molecules and solid materials and there is a rapidly growing interest in SXES in many fields. As, handling biologically-related samples under UHV condition has been successfully test in various conditions, studying biological metals with SXES will become possible in the near future. For this reason, we reported here SXES studies of several Ni(II) / Ni(III) and low spin / high spin Ni(II) complexes which have Ni electronic structures similar with some Ni enzymes.

NiF_2 and NiO are purchased from Sigma-Aldrich and used as purchased (both purity = 99.9%). They are typical high spin Ni(II) and Ni L-edge XAS also indicate they are high spin Ni(II). The complex of $(Ph_4As)_2Ni[S_2C_2(CF_3)_2]$ is a Ni dithiolene which has a low spin Ni(II). Ni L-edge XAS also show a low spin Ni(II) feature. Ni(III)DCB has a low spin Ni(III) centre. Examination of these Ni models will serve as a first step in measuring real biological nickels and will serve as a spectral database used in the future biological spectra analysis. The preliminary resonantly excited SXES experiment on a small number of Ni compounds also confirms the feasibility (shown in Figure 1).



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